

13C N.M.R. and charge distribution in arylcyclobutenyl cations. Part II

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^{13}C N.M.R. AND CHARGE DISTRIBUTION IN ARYLCYCLOBUTENYL CATIONS

Part II¹

BY

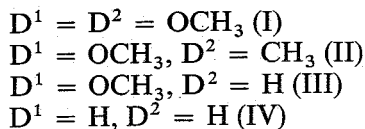
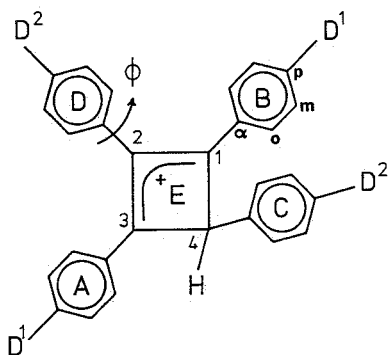
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^{13}C N.M.R. spectra of I, II, III, IV and V have been measured and a number of important assignments made. The resulting chemical shifts are correlated with calculated charge densities. Compound IV has been compared with the tetraphenylcyclobutadiene dication in the literature.

Introduction

It has been established^{1,2}, that ring D in compounds of the general type:



Compounds I-IV

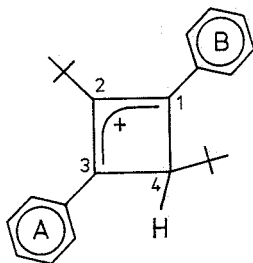
¹ Part, I, Mrs. A. E. van der Hout-Lodder, H. M. Buck and J. W. de Haan, *Rec. Trav. Chim.*, **91**, 164 (1972).

² Miss A. E. Lodder, H. M. Buck and L. J. Oosterhoff, *ibid.* **89**, 1229 (1970).

is turned about 60° out of the plane formed by rings A, B and E. Therefore, most of the positive charge is delocalized in the equivalent rings A and B.

Previously, we reported the UV and PMR spectra² of compounds I-IV and the ^{13}C NMR spectra of I and II (with specific ^{13}C labelling of the cyclobutenyl carbons)¹.

In this paper, a complete and partially revised assignment of the ^{13}C NMR spectra of I and II is given as well as results for compounds III and IV. Moreover, we studied compound V, which results from dissolution of *t*-butylphenylethyne in $\text{SO}_2/\text{HSO}_3\text{F}$ at -70° . In this compound rings A and B are again equivalent (from ^{13}C NMR), but the detailed conformation regarding planarity of the three rings is not known.



Compound V

Spectral assignments

The substituted acetylenes were dissolved in CF_3COOH except for the acetylenes leading to compounds IV and V, which were dissolved in $\text{SO}_2/\text{HSO}_3\text{F}$. Spectra were measured in the FT-mode throughout*. Remeasurement of the specifically ^{13}C -enriched compounds I and II¹ resulted in assignments which differed from those reported previously** for the cyclobutenyl ring. In the FT-spectra we observed three signals with intensities corresponding to an enrichment factor of about 30% near 11 ppm, 46 ppm and 141 ppm (See Table I). From relative inten-

* We gratefully acknowledge the help of Dr. M. J. A. de Bie and Mr. D. Seykens of the University of Utrecht in obtaining the FT spectra.

** Apparently the signals near 73 ppm in our previous CW experiments, although of the right magnitude, must have been due to CF_3COOH . For unknown reasons we never observed the rest of the quadruplet, neither did we find the low-field signals, reported in this study.

Table I

	I	II	III	IV	V
C(1), C(3)	10.88	10.65	11.21	5.51	26.70
C(2)	46.35	45.54	45.71	40.70	14.38
C(4)	140.91	140.56	140.08	140.38	125.50
rings	70.76	70.55	70.71	63.96	68.64
A and B	54.27	54.21	54.17	55.58	55.64
<i>ortho</i>	76.58	76.79	76.66	62.0-65.5	62.95
<i>meta</i>	21.81	22.09	21.89	49.92	53.96
<i>para</i>	137.45	137.56	137.48		
OCH ₃					
ring C,	69.31 ^a	61.29 ^b	62.62-65.0 ^b	58.51 ^b	
ring D	63.87 ^a	62.63 ^b	65.82 ^b	62.03-63.20 ^b	
<i>ortho</i>	77.45 ^a	62.87 ^b	62.62-65.0 ^b	64.20 ^b	
<i>meta</i>	33.06 ^a	52.93 ^a	62.62-65.0 ^b	64.91 ^b	
<i>para</i>	137.87 ^a	65.94 ^b			
OCH ₃	137.98 ^a				
<i>t</i> -butyl C(2) (quat, methyl)					156.94 163.82
<i>t</i> -butyl C(4) (quat, methyl)					159.37 166.58
$J_{13c-13e}$ { 1-2, 2-3	23.4	22.9			
{ 1-4, 3-4	15.1	15.2			

¹³C NMR shifts in ppm upfield from CS₂, measured from acetone-d₆, which was also used as external deuterium lock.

Coupling constants are in Hz.

^a A definite distinction between rings C and D was not made.

^b Specific assignments were not made.

sities and coupling patterns (^{13}C - ^{13}C as well as ^{13}C - ^1H), we assigned these signals to carbon atoms 1 (3), 2 and 4, respectively. The remaining signals were assigned from the spectra of non-enriched compounds.

In compounds III and IV the cyclobutenyl carbons were associated with signals at 11, 46 and 141 ppm and at 5.6, 41 and 141 ppm, respectively.

Assignments in the aromatic region were based on relative intensities, signal multiplicities in off-resonance experiments, known substituent effects³ and analogy relationships. Accordingly, chemical shifts in rings A and B of compound I were carried over to compounds II and III. A clear distinction between signals of rings C and D in compounds I, II and III was not obtained. The *ortho* carbons in all rings are equivalent, which is also the case for the *meta* carbons. This might imply that rotation of rings A and B is possible.

For compound IV all but two aromatic signals were found in a rather narrow range centred at ~ 63 ppm. Specific assignments were not possible, except for the low-field signals.

In compound V, finally, one has to consider the primary substituent effects of *t*-butyl groups for C_2 and C_4 , which are quite different from those of aromatic rings. Therefore, C(4) is found at 125.5 ppm. Assignments for C(1), C(3) (26.7) and C(2) (14.4) were based on relative intensities as well as substituent effects estimated from suitable model compounds. The quaternary carbons resonate near 159 ppm, the corresponding methyl carbons near 166 ppm. The lower field signal (163.8 ppm) is broadened considerably at -70° . Therefore we prefer to assign this signal to the *t*-butyl group at C(2) because the *t*-butyl group at C(4) presumably will experience less sterical crowding and hence may rotate freely. At higher temperatures (-25°), the broadened signals sharpen as a pseudosinglet. We tentatively explain this phenomenon by assuming that at higher temperatures the *t*-butyl group regains its rotational freedom, thus giving rise to a "normal" signal.

Discussion

In principle, ^{13}C NMR chemical shifts contain diamagnetic (σ_d) and paramagnetic (σ_p) terms⁴. Only σ_p may, in fact, be correlated directly with charge densities. In compounds I-IV the substituents are all

³ J. W. Elmsley, J. Feeny and L. H. Sutcliffe, High Resolution NMR Spectroscopy, Vol. II, Pergamon Press Ltd., Oxford, 1966.

⁴ N. F. Ramsey, Phys. Rev., **78**, 699 (1950).

substituted aromatic rings, where σ_d 's will be very similar. In principle, therefore, relative charges in compounds I-IV may be estimated from the shifts.

Generally, calculated charge differences between C(1), C(3) and C(2) amount to about 0.2 units of positive charge corresponding to about 30 ppm chemical shift difference. Taking into account uncertainties in the substituent parameters, one should still be able to detect effects of this order of magnitude with a fair degree of credibility. On the other hand, differences between analogous carbon atoms in compounds I-III are too small and thus irrelevant. The different shifts found in IV should, however, be meaningful because σ_d of a phenyl group will probably not differ too much from those of *para*-substituted phenyl groups.

Some time ago, *Olah*⁵ published results on tetraphenyl- and tetramethyl-cyclobutadiene dications and some cyclopropenium cations. The chemical shifts in these compounds apparently comply with the original rules proposed by *Spiesecke* and *Schneider*⁶ for variously sized aromatic systems. *Olah* did not take into account chemical shift differences resulting from phenyl-substitution of the cyclobutadienyl ring. These effects, however, are of the same order of magnitude as the discrepancies from linearity for some of his results as shown in Figure 2 of ref. 5.

A direct comparison between *Olah's* results for the tetraphenylcyclobutadiene dication (VI) and the spectrum of the tetraphenylcyclobutenyl cation (IV), presented here, reveals some remarkable discrepancies. *Olah* reports broad aromatic signals at 50 and 74 ppm for C_{ortho} , C_{para} and for C_{α} , C_{meta} respectively, while the cyclobutadiene carbons are found at 17.6 ppm.

In the dication, ring carbons 1 through 3 plus the attached phenyl rings should by symmetry contain 1.5 positive charge. In our monocation, we assume that all positive charge is localized at C(1), C(2), C(3) plus rings A, B and C. The sum of all relevant chemical shifts amounts to ~ 1170 ppm in VI and to ~ 1120 in the monocation IV.

If both *Olah's* and our structures as well as the spectral data were correct, one would expect the extra half positive charge to result in a total chemical shift in the dication, which is about 80 ppm lower than for IV. This is certainly not the case, even if we consider the inherent uncertainty in the total chemical shift for IV, caused by the lack of specific assignments. Trying to evaluate the effect of the neutral sp^3

⁵ G. A. Olah and G. D. Mateescu, J. Am. Chem. Soc., **92**, 1430 (1970).

⁶ H. Spiesecke and W. G. Schneider, Tetrahedron Lett., **14**, 468 (1961).

carbon (4) in IV as compared with the half positive sp^2 C(4) in the dication would only tend to make the discrepancy larger.

At this time, we are unable to explain the effects with absolute certainty but we are tempted to suggest, that *Olah* may have observed two rapidly interconverting monocations. The average chemical shift for C(1)–C(3) in IV is about 21 ppm, remarkably similar to the 17.6 ppm found by *Olah* (the extra effect by Br in the possibly interconvertible cations of *Olah* is difficult to assess but it might be of this order). This also means that the aromatic participation in both systems should be similar.

Combining the chemical shifts of I–IV and Fig. 2 in ref. 5, one obtains the experimental charge densities as depicted in Table II. This table also includes revised calculated charge densities, obtained by the SCF method according to *Pariser, Parr and Pople*^{7,8}. Previously¹, a number of models for the calculation were used in order to fit the calculated UV spectra and charge densities with the experimental ones. It now seems that calc. 2 of ref. 1, where all carbon atoms have equal one-centre core integrals and where 1–3 overlap is included shows the best results.

Table II

Compound	% positive charge	
	C(1), C(3)	C(2)
I, II, III	34(28) ^a	12(3) ^a
IV	37(30) ^a	15(5) ^a
V	23	23

^a Between brackets the calculated values are given.

For compound V, we must correct for different σ_d 's of phenyl groups and *t*-butyl groups. One way to achieve this is the study of suitable model compounds like 1-phenylalkanes and 2,2-dimethylalkanes. The difference of about 13 ppm, arrived at in this way seems a fair approximation of the difference in σ_d . In fact, however, one neglects possible slight differences in charge between the appropriate carbon atoms in the model compounds. Nevertheless, we feel that the discrepancies

⁷ R. Pariser, J. Chem. Phys. **21**, 568 (1953).

⁸ R. Pariser and R. Parr, *ibid.* **21**, 466, 767 (1953).

found between V and the other four compounds are significant. The corrected chemical shift for C(2) is 28 ppm, indicating that about the same positive charge is present on C(1), C(3) and C(2). From this, it may be concluded that 1-3 overlap is particularly important in V.

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